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RECRYSTALLIZATION IN ALUMINUM

by

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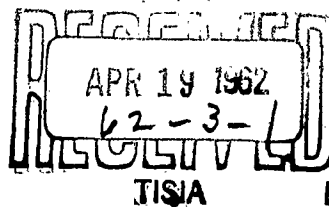
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THE INFLUENCE OF RECOVERY ON RECRYSTALLIZATION IN ALUMINUM*

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ABSTRACT

A description is given of earlier metallographic studies in which the nature and mode of recrystallization in poly-crystalline, zone-refined aluminum containing small quantities of copper was determined from an analysis of the kinetics and geometrical features of the recrystallization process. The isothermal fraction recrystallized at early annealing times obeys the expression

$$X_V = 1 - \exp(-Bt^2)$$

but the rate of recrystallization tends to be retarded as annealing proceeds. This is shown to be due to a decrease in the isothermal grain-boundary migration rate with time during annealing. The effect is more pronounced the lower the anneal-ing temperature for a specific copper content.

Microcalorimetric studies of the release of stored energy in these aluminum alloys have shown that the decreasing growth

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rates result from competing recovery processes which lower the deformation energy in unrecrystallized portions of the samples undergoing recrystallization.

In agreement with the results of previous investigations on recovery in aluminum, the patterns of stored energy release found reveal that there are two distinct recovery stages in the annealing of these aluminum-base materials. Possible mechanisms responsible for the two recovery stages are discussed.

INTRODUCTION

When a metal is plastically deformed by cold working, a certain fraction of the mechanical energy expended in performing the deformation is retained and is stored in the metal in the form of various types of imperfections while the remainder is converted into heat.[1] The energy thus stored in the metal renders it thermodynamically unstable relative to the unstrained, well-annealed condition. If thermal energy is imparted to allow sufficient atomic mobility, there will be a tendency for the deformed metal to return again to the lower energy, annealed state. Accompanying such an approach toward equilibrium will be a release of the stored energy of deformation. The various processes by which the annealed state is reached are classified into two categories-recovery and recrystallization. In this paper, the term recovery is used to encompass all those annealing phenomena which in a given region precede recrystallization, the latter being defined as the appearance of comparatively strain-free grains separated from the deformed matrix or other

recrystallized grains by high-angle grain boundaries.

The present paper is the second in a series of three dealing primarily with the processes of recovery and recrystallization in polycrystalline, zone-refined aluminum and in binary alloys of this aluminum with minute quantities of copper. The emphasis in this paper will be placed on the influence recovery can exert on the kinetics of recrystallization and on the rate of grain-boundary migration. A complete description of the experimental techniques used in the preparation, fabrication, deformation, annealing, and evaluation of the zone-refined aluminum alloy containing 0.0034 at. % copper was given in the first paper.[2] The same methods have been employed for the other compositions studied. All were fabricated to a penultimate grain size of 0.5 mm and were deformed prior to the recrystallization studies by rolling at $0^{\circ}C$ to a reduction in thickness of 40%.

THE NATURE OF RECRYSTALLIZATION IN ALUMINUM

The kinetics of isothermal recrystallization are generally described in terms of the phenomenological equation

$$X_v = 1 - \exp(-Bt^k) \qquad (1)$$

where X_v is the volume fraction of material recrystallized during the time, t, and B and k are constants which depend on the nature of the model taken for nucleation and growth in recrystallization. Figure 1, taken from the first paper in this series[2], is a plot of log $\ln \dfrac{1}{1 - X_v}$ versus log t for recrystallization in the alloy of zone-refined aluminum contain-

ing 0.0034 at. % copper.   That these recrystallization data do follow an equation of the form of Eq. (1) over the range of annealing times and temperatures studied is revealed by the straight-line curves of Fig. 1.   The value of k determined from the slopes of these lines is approximately 2.   This may be compared with k values ranging from 1 to 2 found in previous recrystallization studies on aluminum by Perryman[3,4] and Laurent and Batisse.[5]   The geometrical and other details of recrystall-ization found for the zone-refined aluminum alloy containing 0.0034 at. % copper[2] may be summarized as follows:

a.   The recrystallized regions were nucleated as colonies of contiguous grains strung out along the deformed matrix grain edges (inter-section of three matrix grain boundaries);

b.   All colonies formed at annealing times sufficiently short to be considered to be zero and no further isothermal nucleation took place during the experimental annealing times employed;

c.   Only a small fraction--about 0.05--of the total available matrix grain edges produced colonies;

d.   Each colony had virtually its full length--the length of the nucleating edge--at birth;

e.   After nucleation, growth proceeded only in two dimensions perpendicular to the nucleating matrix grain edge, the third growth dimension being stunted by impingement of the nuclei in a direction parallel to the grain edge; and

f.   At a given annealing temperature, growth rates varied

from colony to colony; the maximum rate was approximately 12 times the minimum rate.

This interpretation was based on the observed kinetics, on measurements showing that the isothermal rate of growth of the recrystallization nuclei was approximately independent of time during the time periods studied, and on a considerable amount of additional corroborating and self-consistent metallographic data of both a qualitative and quantitative nature. In addition, all the rate quantities that were measured were found to be characteristic of the same basic process-- the growth or boundary migration--process, including the constant B in Eq. (1) which, based on this model for recrystallization, is proportional to the square of the growth rate.

It is interesting to note in this connection the work of Weissmann[6] on subgrain growth in 99.998% purity, polycrystalline aluminum cold rolled 81.7%. By combining metallographic techniques with x-ray microscopy and diffraction analysis, he was able to follow the emergence of certain subgrains from a cluster of subgrains by the process of subgrain growth. Weissmann found that recrystallized grains are the product of this preferential subgrain growth. He further noted that the fastest growing subgrains which also subtend large disorientation angles with respect to their neighbors derive from regions associated with the grain edges of the deformed matrix. These observations of Weissmann provide evidence concerning the nuclei for recrystallization and add support to the picture of edge-nucleated, growth-controlled recrystallization in aluminum presented above.

RETARDATION OF RECRYSTALLIZATION

In the preceding section, it was indicated that the kinetics of recrystallization in an aluminum alloy containing 0.0034 at. % copper could be described reasonably well by the equation

$$X_v = 1 - \exp - (Bt^2) \qquad (2)$$

over virtually the entire range of time and temperature studied, from about 0.002 to 0.1 fraction recrystallized. A metallographic analysis of the kinetics of recrystallization in the zone-refined aluminum, however, revealed that Eq. (2) is valid only over a very limited range for this material. This is illustrated in Fig. 2, which is a plot of log $\ln \frac{1}{1 - X_v}$ versus log annealing time for five different annealing temperatures. At an annealing temperature of $64.5^\circ C$, the data in the zone-refined aluminum follow the straight-line behavior predicted by Eq. (2) for values of $X_v < 0.10$, but thereafter appear to digress somewhat from the expected straight line toward longer annealing times. As the annealing temperature is lowered, the departure from linearity--equivalent to a retardation of the recrystallization--becomes more obvious and begins earlier in the recrystallization process, i.e., at smaller values of X_v. At the lowest temperature, $0.1^\circ C$, the effect manifests itself at values of X_v of less than 0.01.

Examination of the kinetics of recrystallization in the other compositions investigated (0.00021, 0.00043, 0.0017,

0.0068, 0.0124, and 0.0256 at. % copper) revealed that this
retarding effect is quite general, as illustrated in Figs.
3 and 4 for the 0.0017 and 0.0068 at. % copper alloys,
respectively. It may be noted that the retarding effect is
quite marked in the 0.0017 at. % copper alloy (Fig. 3), where-
as it manifests itself only slightly in the 0.0068 at. %
copper alloy (Fig. 4). The 0.0034 at. % copper alloy appears
at first glance to be an exception. A close examination of
the recrystallization kinetic curves of Fig. 1 reveals that
the slope of $125^\circ C$ curve is slightly less than the slopes of
the curves for the higher annealing temperatures. This lower
slope is undoubtedly a manifestation of the retarding effect
in this alloy. If an annealing temperature lower than $125^\circ C$
had been chosen, this alloy, too, would very probably show a
more marked retarding effect.

An explanation of this retarding effect may be sought
most readily in either a change in the mode of recrystalliza-
tion or in a decrease in the rate of growth of the recrystalli-
zed grains with annealing time. Quantitative metallographic
studies similar to those performed on the aluminum alloy
containing 0.0034 at. % copper revealed that the mode of
recrystallization in the zone-refined aluminum and in the other
aluminum-copper alloys is similar to that outlined in the
previous section of this paper. This is true not only during
the time period in which the recrystallization data obey
Eq. (2), as, for example, in the early part of the curves in
Fig. 2, but also in the periods where the retarding effect

manifests itself. Thus, the effect cannot be accounted for by a change in the mode and geometrical features of recrystallization.

It was found, on the other hand, that in the compositions which exhibited appreciable retardation effects, the isothermal rate of growth was not independent of annealing time over the entire temperature range. Typical growth curves are shown in Figs. 5 and 6 where p, the average diameter of the largest recrystallized grain, is plotted as a function of annealing time for the different annealing temperatures in the zone-refined aluminum and in the alloy containing 0.0017 at. % copper, respectively. A comparison of the curves in Figs. 2 and 5 and in Figs. 3 and 6 reveals a significant similarity in the behavior of the recrystallization data (X_V curves) and that of the growth data (p versus t curves, the slopes of which are directly proportional to the linear growth rates). For example, in the zone-refined aluminum at annealing temperatures of 76.5 and $64.5^{\circ}C$ where the p versus t data* are approximately linear, i. e.,the growth rates are constant, the X_V data obey Eq. (2). On the other hand, at 38.7, 24.0, and $0.1^{\circ}C$, where the X_V curves digress from the straight-line behavior predicted by Eq. (2), the p versus t curves are no longer linear over the range studied. The instantaneous

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* The measurements of p were carried out only to about $X_V = 0.10$ and, therefore, the growth rates could be determined only up to that point.

The instantaneous slope of these p versus t curves falls off with time indicating that the rate of growth decreases as a function of annealing time. Furthermore, it is seen in Figs. 5 and 6 that the lower the annealing temperature, the more marked is the decrease in growth rate, also in accordance with the recrystallization data of Fig. 2.

The experimental studies on the kinetics of recrystallization in these dilute aluminum-copper alloys may be summarized as follows:

a. There is a retardation of recrystallization which is quite general in these alloys and is manifested by deviations from the expected kinetic behavior predicted by Eq. (2);

b. This effect appears to become more marked as the copper content of the alloy is decreased;

c. For a given alloy content, the retarding effect becomes more pronounced the lower the annealing temperature; and

d. The decrease in the rate of growth (boundary migration) of the recrystallized grains with annealing time is responsible for the retardation of recrystallization.

COMPETITION BETWEEN RECOVERY AND RECRYSTALLIZATION

The growth of a recrystallized grain is motivated by the stored energy of deformation that is present on the unrecrystallized side of the migrating grain boundary. If the amount of stored energy per unit volume of unrecrystallized material is continually decreased during the course of

recrystallization by competing recovery phenomena, then the instantaneous rate of growth (boundary migration) should also decrease. That this is in fact the explanation for the decrease in growth rates observed in connection with the retarding of recrystallization was shown by making isothermal calorimetric measurements of the release of stored energy during annealing. These measurements were carried out on several samples of the zone-refined aluminum alloys containing 0.0068 and 0.0017 at. % copper which were carefully prepared so that they were as nearly identical as possible to those used in the metallographic work. The calorimetric techniques have been described elsewhere.[7-9]

The results of calorimetric measurements on a deformed sample of the 0.0068 at. % copper alloy annealed at 170°C are presented in Fig. 7. Here the rate of stored energy (heat) evolution, P, is plotted as a function of annealing time, t, in linear coordinates. The most striking feature of this curve is that the rate is initially high and gradually decreases to zero. This behavior is typical of recovery type kinetics. However, according to the metallographic data in Fig. 4, recrystallization, which is expected to have nucleation and growth type kinetics, is proceeding at this same temperature during the time period of the calorimetric measurements. The manifestation of recrystallization is not obvious from the energy release data of Fig. 7. This is quite different from the case of high-purity copper, studied by Gordon,[8] where a distinct peak of energy release corresponding to re-

crystallization was found. A somewhat more revealing plot
of the calorimetric data of Fig. 7 is shown in Fig. 8 where
log P is plotted as a function of log t. Here it becomes
apparent that there is actually an appreciable change in
shape of the curve at about 0.5 hr. This change occurs at a
point where, according to metallographic observation,
recrystallization is beginning to manifest itself. In
addition, the time at which the rate of stored energy
evolution becomes approximately zero in Fig. 7 corresponds
roughly to the time when recrystallization would be expected
to be essentially completed. It seems likely, therefore, that
the kinetics of energy release shown in Figs. 7 and 8
correspond to recrystallization superimposed on other heat
evolving processes (recovery). A separation of the recrystalli-
zation portion of the experimental curve by a somewhat
arbitrary extrapolation of the first and last segments of the
curve is depicted in Fig. 9.

In order to obtain a clearer picture of the patterns of
stored energy release in this 0.0068 at. % copper alloy of
aluminum, a second deformed sample was given a series of low-
temperature, pre-recrystallization anneals before a final
recrystallization anneal in the calorimeter at $170^{\circ}C$.* Figure
10 shows the pattern of energy release obtained in this

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* The low-temperature anneals were also carried out
isothermally in the calorimeter in an attempt to obtain infor-
mation regarding the release of stored energy during recovery.
The details of these experiments are presented later.

specimen at 170°C. At short times, there is an initially
high rate of energy evolution which decreases rapidly to
zero. This is followed by a behavior typical of the
recrystallization process in that the rate increases from
zero to a maximum and then decreases to zero again. It is
clear from these data that the eecrystallization process
in this alloy can be largely separated from other energy-
releasing phenomena when by low-temperature annealing, an
extended amount of recovery is allowed to precede
recrystallization.

The initially rapid decrease to zero rate of the energy
release in Fig. 10 is evidence that the recovery processes
are virtually completed as a result of the low-temperature
anneals. This suggests that the recrystallization observed
in this sample at 170°C proceeded with a driving force which
is essentially constant during annealing. The kinetics of
recrystallization, therefore, should obey Eq. (2). Accord-
ingly, in Fig. 11, $\log \ln \frac{1}{1 - X_E}$ is plotted versus log
annealing time where X_E is the fraction of the stored energy
of recrystallization released in time, t, as determined from
the calorimetric data in Fig. 10. Also plotted in Fig. 11
for the sake of comparison is the metallographically determined
recrystallization data at the same temperature (170°C) taken
from Fig. 4. It is seen that the energy release data follow
a straight-line curve with a slope of 2 up to about $X_E = 0.5$
in accordance with the prediction of Eq. (2). Beyond $X_E = 0.5$
in Fig. 11, the experimental data again deviate from Eq. (2)

even though presumably no recovery is occurring. In almost
all cases in which the kinetics of recrystallization have
been reported in the literature, this type of behavior is
manifested at long annealing times. Examples of this are
seen in the recrystallization data of Gordon[8] on copper,
and of Perryman[4] on aluminum. This effect may be a result
of inhomogeneities in the original deformation. It is,
for example, not unreasonable to expect the deformation to
be somewhat higher near the boundaries of the matrix grains
than near the centers of the grains especially where the
initial grain size is rather large as is the case in these
materials. Since the recrystallized grains are much smaller
than the originally deformed grains and since they are
nucleated along the matrix grain edges, then during the early
stages of recrystallization the recrystallized grains would
be growing mainly in regions near the grain boundaries of the
deformed grains. At later stages, however, when the re-
crystallized grains are larger in size, they would be growing
mainly in regions that are in the centers of the deformed
grains. Thus, a somewhat lower driving force would be ex-
pected during the later stages of recrystallization than in
the early stages and a bending over of the kinetic data would
result. Figure 11 also shows that the recrystallization
curve determined from the calorimetric data is displaced
slightly with respect to the metallographic data toward
longer annealing times. It must be remembered in this connec-
tion that the calorimetric sample had undergone a substantial

recovery treatment prior to recrystallization, whereas the metallographic data was obtained from samples in which no such recovery anneals were given. Therefore, a lower driving force is expected to be present in the calorimetric sample as compared to the metallographic samples. Calculations of the stored energy of recrystallization, based on the data of the two calorimetric runs described earlier, substantiate this. In the sample which had undergone a great deal of prior recovery, a value of 0.70 cal/mole was obtained. This may be compared to 1.10 cal/mole for the case where no low-temperature recovery anneals were given.

From the calorimetric measurements thus far reported, it is evident that recovery and recrystallization are overlapping processes in these aluminum-base materials and that they compete with each other for the stored energy of cold work. It might appear then, that especially at the higher annealing temperatures, there is a certain inconsistency between the kinetics of recrystallization determined by metallographic techniques and the observation that recovery occurs concurrent with recrystallization and would thus be expected to lower the driving force for recrystallization in unrecrystallized regions. For example, if the driving force per unit volume of unrecrystallized material is lowered as recrystallization proceeds, then the straight-line prediction of Eq. (2) should never hold as it does at $170^\circ C$ in the 0.0068 at. % alloy (see Fig. 4). A calculation, however, shows that during the time interval where metallographic data

was taken at $170^{\circ}C$ (720-5400 sec), the instantaneous stored
energy (driving force) per unit volume of unrecrystallized
material is only decreased from 1.15 to 1.10 cal/mole. This
small change is not sufficient to manifest itself in the
kinetic data since the effect of this change is well within
the experimental scatter of the metallographically determined
fraction recrystallized. Accordingly, no deviation from
Eq. (2) was observed at $170^{\circ}C$. On the other hand, after
annealing a sample at $139^{\circ}C$ for 180,000 sec ($X_v = 0.08$),
a driving force of only 0.7 to 0.8 cal/mole still remains.
This represents a significant decrease in the driving force,
about 25 or 30%, and, correspondingly, some deviation from
Eq. (2) was observed at this temperature in the metallographic
study (see Fig. 4.).

Calorimetric measurements carried out on deformed samples
of the aluminum alloy containing 0.0017 at. % copper produced
stored energy evolution curves which exhibited qualitatively
much the same behavior as those already shown for the 0.0068
at. % copper alloy. Figure 12, for example, is a plot of log
P versus log t for a sample of this alloy annealed in the
calorimeter at $145^{\circ}C$. The characteristics of the curve in
Fig. 12 are very similar to those of the curve for the evolution
of stored energy shown in Fig. 8 for the 0.0068 at. % copper
alloy.

A second deformed sample of the 0.0017 at. % alloy was
annealed in a calorimeter for 10 1/2 hr at $125^{\circ}C$ and subsequently
reannealed in the calorimeter at $145^{\circ}C$ until recrystallization

was complete. Figure 13 is a plot of the rate of stored energy evolution, P, as a function of annealing time for this sample at the two temperatures. The instantaneous stored energy, $E_p(t)$, still remaining in the sample after annealing to time, t, can be calculated from this type of data by using the equation

$$E_p(t) = \int_t^{t_{end \ of \ recrystallization}} P dt. \qquad (3)$$

Table I lists the values of $E_p(t)$ for several different annealing times at 125°C obtained from a graphical integration of the curves in Fig. 13. Also Listed in Table I is the volume fraction recrystallized, X_v, at these same annealing times and the instantaneous driving force for recrystallization, $Z(t)$ where

$$Z(t) = \frac{E_p(t)}{1 - X_v}. \qquad (4)$$

It is seen from Table I that the driving force for recrystallization is reduced by one-third as recrystallization proceeds from about 0.1 to 10%. Correspondingly, there is appreciable deviation from the straight-line prediction of Eq. (2) in the $\log n \frac{1}{1 - X_v}$ versus $\log t$ plot for this alloy at 125°C in Fig. 3.

On the basis of the evidence already presented, it is apparent that Eq. (2) can describe the kinetics of re-crystallization in these aluminum alloys accurately only if the driving force for recrystallization remains essentially constant during annealing. However, because of the edge-

nucleated, growth-controlled mode of recrystallization
in these aluminum alloys, the quantity B in Eq. (2) should
be proportional to the square of the rate of growth of the
recrystallized grains.[2] Since the rate of growth is
directly proportional to $Z(t)$, the driving force for
recrystallization, we can write Eq. (2) as

$$X_V = 1 - \exp - [CZ(t)t]^2 \qquad (5)$$

where C is a constant. Equation (5) suggests that if log
$\ln \frac{1}{1 - X_V}$ is plotted versus log $[Z(t) \cdot t]$ a straight line
with a slope of 2 should result regardless of changes in
the driving force. Such a plot is presented in Fig. 14
for recrystallization at $125^{\circ}C$ in the 0.0017 at. % copper
alloy, using the values of $Z(t)$ listed in Table I. Also
shown in Fig. 14 for the sake of comparison is the usual
log $\ln \frac{1}{1 - X_V}$ versus log t recrystallization plot at $125^{\circ}C$
for this alloy. It is seen that whereas the latter plot
exhibits a deviation from the straight-line kinetic behavior
the plot of $[Z(t) \cdot t]$ produces a linear curve over the
entire range studied. The slope of this line is about 2,
in accordance with Eq. (5).

The results of the calorimetric experiments which were
performed on these two alloys of zone-refined aluminum
establish with little doubt that recovery and recrystallization
are overlapping annealing processes in these materials.
Furthermore, substantial amounts of the stored energy of
cold work are released by one or more recovery mechanisms

Table I. Driving Force for Recrystallization as a Function
of Annealing Time at 125°C

Annealing Time (sec)	Instantaneous Stored Energy, $E_p(t)$ (cal/mole)	Volume Fraction Recrystallized X_v	Instantaneous Driving Force for Recrystallization $Z(t)$ (cal/mole)
3600	0.93	8×10^{-4}	0.93
4800	0.90	5.1×10^{-3}	0.90
6000	0.87	7.1×10^{-3}	0.88
7200	0.85	1.6×10^{-2}	0.86
10 800	0.78	1.9×10^{-2}	0.79
13 200	0.73	2.4×10^{-2}	0.75
18 000	0.66	5.4×10^{-2}	0.70
32 000	0.56	9.3×10^{-2}	0.62

during, as well as prior to, recrystallization. As a
result of this competition, the driving force for re-
crystallization does not remain constant during the anneal-
ing experiments of this investigation. Evidence has been
presented which shows that this decrease in driving force
is responsible for the retarding of the kinetics of re-
crystallization and thus, the observed decrease in growth
rates with annealing time.

The retardation of recrystallization by simultaneous
recovery is very probably a general phenomenon. Leslie,
Plecity, and Michalak,[10] for example, observed that the
rate of growth of recrystallized grains in iron and iron-
manganese alloys also decreased with time during recrystal-
lization. They indicated that the probable cause for this
decrease was a lowering of the residual strain energy
per unit volume of the deformed metal because of recovery
occurring simultaneously with recrystallization. They
presented softening curves based on hardness measurements
which substantiated that such recovery was taking place.
Perryman[4] also found that the rate of linear growth of
recrystallization grains in high-purity aluminum was not
constant but decreased with time after about 3% recrystal-
lization. In addition, Perryman[11] observed that sub-
structural changes occur during annealing which are
accompanied by a decrease in hardness. He showed this to
proceed both before,and at the same time as, recrystallization.
Assuming that the edge-nucleated, growth-controlled model

for recrystallization was operative in these experiments, these facts would account for the somewhat low value that was observed by Perryman[3,4] for the kinetic constant k of Eq. (1).

The influence of recovery on recrystallization is, however, undoubtedly more effective in some instances than in others. Whereas in high-purity aluminum and perhaps in iron also, the effect is strong, in high-purity copper,[8] it appears to be relatively inconsequential. Basically, of course, the strength of the effect is determined by the relative rates of recovery and recrystallization. Factors such as purity, the amount and temperature of deformation, prior grain size, and the nature of the metal itself all will presumably alter the magnitudes of the rates of re-covery and recrystallization. Since, in general, recovery phenomena have lower activation energies than does re-crystallization, low temperatures will favor recovery over recrystallization. Thus, the retarding effect should be greater at the lower annealing temperatures in a given material, as has been found in the work reported in this paper.

The effect of impurity content on the retardation of recrystallization by simultaneous recovery is somewhat less straight forward. The statement made earlier that the re-tardation noted became more pronounced for the lower copper contents, might appear to indicate that high purity favors recovery over recrystallization. A different picture

emerges, however, if the recrystallization data are examined

for varying copper content <u>at fixed annealing temperatures.</u>

This may be done with the*and of the*curves in Fig. 15 where the

fraction of recrystallization at the beginning of retardation,

(taken as the point in the kinetic data where noticeable

deviations from Eq. (2) were first observed) is plotted as

a function of annealing temperature for different composi-

tions of copper in aluminum. It is to be noted in Fig. 15

that <u>for a given annealing temperature</u> the retarding effect

sets in at lower and lower values of X_v, the fraction re-

crystallized, <u>as the impurity content is raised.</u> Thus, it

becomes clear that the retarding effect is in fact less,

rather than more, marked as the impurity level is lowered, and

that high purity favors recrystallization over recovery.

This phenomenon may be rationalized by the hypothesis that

the addition of impurities decreases recrystallization

rates more rapidly than recovery rates. Some evidence for

this view is suggested by the variation in the activation

energies for recovery and recrystallization as a function

of impurity content. Estimates of the activation energies

for recovery were obtained by plotting the times for the

start of retardation, as a measure of recovery rates, versus

the reciprocal of the absolute temperature. The activation

energy for recovery, determined in this manner, was found

to increase from about 13,000 to 19,000 cal/mole as the

copper content of the alloys went from zero to 0.0068 at. %.

Thus, the recovery rate undoubtedly decreases with impurity

additions. For the same range of copper composition,
however, the activation energy for recrystallization is
increased from 15,000 to about 30,000 cal/mole.[ref 12]
Consequently, the rate of recrystallization decreases
much faster than that of recovery as the copper content
is raised. The result is that recovery is favored over
recrystallization as copper is added.

The calorimetric work of Clarebrough, Hargreaves,
and West[13] on copper seem to support this view. These
investigators found that the ratio of pre-recrystallization
energy release to that during recrystallization is consider-
ably higher for impure copper than for a somewhat higher
purity copper. This probably means that the impurities
decrease the recrystallization rates more than the recovery
rates, so that, again high purity favors recrystallization
over recovery.

Recovery in Aluminum

As was briefly mentioned earlier, a deformed sample
of the aluminum alloy containing 0.0068 at. % copper was
annealed in a calorimeter at a series of temperatures below
that necessary for recrystallization. By making calori-
metric measurements at these low temperatures, information
regarding the patterns of stored energy release during
recovery was obtained. Figure 16 is a plot of the rate of
stored energy evolution as a function of the reciprocal of
the annealing time at $65°C$ for this deformed sample. The

The rate in this case is a hyperbolic function of annealing time as evidenced by the straight-line curve passing through the origin. The total stored energy released during this stage was 0.36 cal/mole. Subsequent annealing at 92 and 122°C produced no release of stored energy within the limits of detectability (estimated to be 0.02 cal/mole). During annealing at 139°C, a second energy release was observed with kinetics different from those found at 65°C. In this case, the rate of stored energy evolution was approximately proportional to the reciprocal of the annealing time squared as shown in Fig. 17. The total energy evolved at 139°C was 0.26 cal/mole. Subsequent annealing of this same specimen at 170°C produced recrystallization as discussed earlier.

Astrom[14] also observed two distinct patterns of stored energy release prior to recrystallization in compressed 99.99% polycrystalline aluminum. As in the present experiments, Astrom's measurements were made isothermally at successively raised temperatures in the range 70-350°C. The samples were, therefore, in the cold-worked state only at the lowest annealing temperature. The first stage of energy release observed by Astrom occurred below 100°C and exhibited hyperbolic rate curves. The second pre-recrystallization energy release which Astrom detected, manifested itself at temperatures above about 180°C and displayed exponential rate kinetics. From the time constants of the exponential rate curves for two equally deformed samples measured at different temperatures, Astrom calculated an energy of

activation for the high-temperature recovery process of
36,000 cal/mole. Astrom observed further that there were
certain changes in the substructure of the metal which
accompanied this high-temperature, pre-recrystallization
energy release. He suggested that the process was either
a growth of subgrains or polygonization, but the evidence
did not allow a definite conclusion.

Cherian, Pietrokowsky, and Dorn[15] observed two distinct
recovery processes in polycrystalline, commercially pure
aluminum tensile specimens previously strained 9.2% at room
temperature. Following a recovery treatment at low tempera-
tures ($<100°C$), these workers found a significant lowering
of the initial flow stress upon restraining. After an
additional strain of about 4%, the flow stress was restored
to essentially that value which would have been obtained if
the specimen had not been given the recovery anneal. This
the authors called metarecovery. At higher recovery
temperatures (150-200°C), Cherian et al. observed not only
metarecovery, but also a permanent decrease in the flow
stress of the recovered material from that of unrecovered
material at the same total strain for all strains. This was
called orthorecovery. The kinetics of meta-and orthorecovery
observed in these experiments were reported to be distinctly
different and it was indicated that orthorecovery occurred
more slowly than metarecovery. An activation energy for
orthorecovery of 33,000 cal/mole was found.

The metallographic and x-ray observations of Perryman[11]

on the substructure of polycrystalline specimens of
aluminum deformed at room temperature are also consistent
with two stages of recovery. Perryman observed that
recovery at temperatures as low as room temperature pro-
duced much sharper substructures than were present directly
after deformation. In addition, certain of the deformation
bands appeared to have split up into equiaxed regions of
about 1 to 2μ in size. Perryman found that recovery at
high temperatures (near recrystallization temperatures)
produced structural changes much the same as those at the lower
temperatures. In addition, however, he noted that at these
higher temperatures, the equiaxed subgrain size was somewhat
larger (4μ); in fact, certain areas produced very large
subgrains (10 to 30μ). He also noted that these changes
of substructure were accompanied by a substantial decrease
in hardness.

It is tempting now to discuss from a mechanistic view-
point the stages of evolution of stored energy which were
observed during the recovery of the zone-refined aluminum
alloy containing 0.0068 at. % copper. As a starting point,
it is necessary first to consider the nature and structure
of the cold-worked state. Gay, Hirsch, and Kelly[16] have
investigated the deformed state in a number of metals by
means of an x-ray microbeam technique which allowed a
resolution of diffraction spots originating from very small
domains. They concluded that after sufficiently heavy
deformations, a cellular or subgrain structure is formed

consisting of regions of relatively low dislocation density separated by highly distorted boundary regions containing a high dislocation density. They proposed that the formation of a structure of this kind is a direct result of the accumulation of dislocations on slip bands during cold work and is not due to a recovery process subsequent to cold working. For aluminum deformed 57% by rolling at room temperature, the order of magnitude of these subgrains was about 1 or 2 μ with a mean angle between them of 3 deg. Further evidence establishing the existence and size of these subgrains has been presented by Heidenreich[17] and Hirsch, Horne, and Whelan[18] based on electron transmission microscopy studies of thin aluminum foils.

In this connection, the photomicrograph shown in Fig. 18 is interesting. This photomicrograph, taken under polarized light at 250X, illustrates the growth of a re-crystallized grain (lower right) into the deformed matrix in an aluminum-copper alloy--the deformed matrix being characterized by the banded regions of light and dark shading. The more or less abrupt change from light to dark in the deformed area is, under polarized light, indicative of a change in orientation and suggests, therefore, the presence of a boundary or wall. Close examination of the photomicrograph in Fig. 18 reveals that the maxima in the protrusions of the recrystallized grain into the deformed matrix occur where there is an abrupt change in shading (presence of a wall) in the deformed region. The shape of the migrating

boundary of the recrystallized grain implies that these walls in the deformed material are preferred regions for growth of the recrystallized grain. This in turn suggests that there is a higher dislocation density and therefore a higher driving force for growth in these wall regions. Although the relationship between the banded regions of the photomicrograph and the subgrain structure mentioned earlier is not apparent, these observations would seem to support the view that cell walls contain a large part of the stored energy of deformation.

Gay, Hirsch, and Kelly[16] were led to conclude from their x-ray microbeam studies that recovery is due to a rearrangement of dislocations in the subgrain boundary regions and the possible movement of dislocations from the subgrain interior to the boundaries. Perryman[11] suggested the latter as an explanation of the substructural changes he observed during recovery of aluminum.

According to the definition of recovery used in this paper, subgrain growth must also be listed as a recovery mechanism. Small increases in subgrain size were detected by Perryman[11] during the recovery annealing of deformed aluminum at temperatures near the recrystallization temperature. Ricketts, Kelly, and Beck[19] studied the kinetics of subgrain growth in rolled single crystals of aluminum by means of electron microscopy. They found that subgrain growth was responsible for significant changes in hardness under conditions where no recrystallization was taking place.

Weissmann[6] investigated both the kinetics and orientation
dependence of subgrain growth in polycrystalline aluminum
cold rolled 81.7%. He noted that certain subgrains, which
were highly misoriented with respect to neighboring sub-
grains, grew very rapidly. These presumably would correspond
to the recrystallized grains observed by Vandermeer and
Gordon.[2] On the other hand, Weissmann[6] found that subgrains
misoriented only slightly with respect to their neighbors
(1 deg or less) could also grow to rather larger sizes
($\succ 50 \mu$). These subgrains, however, exhibited very slow
growth rates compared to the others.

It is suggested now that the recovery of the deformed
alloy of aluminum containing 0.0068 at. % copper occurs by
the following mechanisms: The first stage of recovery at
65°C involves both the reduction of dislocation density
within the subgrains and the rearrangement of the dis-
locations located in subgrain boundary regions. The second
recovery stage in this alloy occurs at 139°C and is thought
to be the result of a slow, gradual growth of subgrains
subtending small misorientation angles with respect to their
neighbors.

Although the correctness of this model cannot be con-
clusively proven at the present time, there is some experi-
mental evidence which might be considered to lend support
to it. For example, the model implies that after a recovery
anneal at 65°C, virtually all the remaining strain energy is
contained in the surface energy of the sub-boundaries.

Therefore, E_p, the stored energy per mole which still remains can be written as

$$E_p = \frac{K6V}{D} \qquad (6)$$

where K is a constant between 1 and 3, D is the average subgrain size, 6 is the average specific subgrain boundary energy, and V is the molar volume of the metal. It is assumed now that the subgrain surface energy, 6, can be roughly estimated using the equation given by Cottrell[20],* for a symmetrical boundary containing edge dislocations namely

$$6 = \frac{\mu b}{4\pi(1 - \gamma)} \Theta(A - \log \Theta) \qquad (7)$$

where μ is the shear modulus of the material, b is the Burgers vector, A is a constant of magnitude about 0.5, (ref 20) γ is Poisson's ratio, and Θ is the mean angle between subgrains. Using the value for aluminum of $\Theta = 3$ deg. from the work of Gay et al.[16] and taking $V = 10$ cm^3/mole, $\mu = 2.7 \times 10^{11}$ dyne/cm^2, b = 2.85 x 10^{-8} cm, $\gamma = 0.33$, $D = 1\mu$, and K = 2, an estimate for E_p of about 0.75 cal mole is obtained using Eqs. (6) and (7). This may be compared with a value of about 0.95 cal/mole determined from the stored energy measurements reported in this paper. Of course, only the order of magnitude of the calculated value is significant

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* It should be pointed out that this equation is strictly applicable only to simple tilt boundaries and therefore its application here must be taken with some reservation since it is probable that the subgrain boundaries are not all simple tilt boundaries.

in view of the assumptions made. The agreement between calculated and experimental values, however, does give one some degree of confidence in the idea that at this point in the annealing process, the remaining stored energy is contained virtually entirely in the surface energy of the sub-boundaries.

If the recovery process that occurs at $139^{\circ}C$ is sub-grain growth, then the rate of release of stored energy, P, should be given by

$$P = - \frac{dE_p}{dt} = \frac{K6V}{D^2} \frac{dD}{dt} \qquad (8)$$

which is obtained by differentiation of Eq. (6).* There is some evidence that the increase in subgrain size in aluminum may be a linear function of annealing time. Both Weissman[6] and Towner and Berger[21] have observed linear rates for sub-grain growth in aluminum. If it is assumed now that the subgrain size increases linearly with annealing time during recovery at $139^{\circ}C$, then D is proportional to t, dD/dt is constant and, according to Eq. (8), P would be proportional to the reciprocal of the annealing time squared. Just such kinetics have been observed for the release of stored energy during recovery at $139^{\circ}C$ in the aluminum alloy containing 0.0068 at. % copper (See Fig. 17). Thus, the experimental results at $139^{\circ}C$ can be plausibly interpreted in terms of a

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* Equation (8) as written assumes that the specific subgrain surface energy remains unchanges as subgrain growth takes place.

subgrain growth mechanism for recovery. These results, however, do not preclude the possibility that an alternate mechanism can be evoked having similar kinetics. Even though there is no direct evidence for the subgrain growth mechanism in the present work, the studies of Weissmann[6], Perryman,[11] Ricketts et al.,[19] and Towner and Berger[21] on subgrain growth in aluminum provide some degree of justification for adopting this mechanism for recovery at 139°C.

SUMMARY

1. The kinetics of isothermal recrystallization in dilute, polycrystalline alloys of copper in zone-refined aluminum cold rolled 40% at 0°C obey the equation

$$X_v = 1 - \exp - (Bt^2)$$

   under annealing conditions for which the driving force for recrystallization is essentially constant.

2. The rates of isothermal recrystallization have bee found to be retarded under special conditions in certain of the alloys which thus show deviations from the rate law given above.

3. For a given purity, the deviations are greater the lower the annealing temperature, whereas for a given annealing temperature the deviations are more marked the higher the impurity content.

4. The retarding effect has been found to be a result of a decrease in the linear rate of growth of the recrystallized grains as a function of annealing time.

5. It has been shown by means of calorimetric measurements of the evolution of stored energy that recovery and recrystallization overlap to a large extent in these aluminum-base alloys. As a result, the driving force for recrystallization is continually being decreased by recovery. The deviations from the kinetic equation given in No. 1 above have been found to be a result of this decrease in driving force

6. Increasing impurity content has been found to favor recovery over recrystallization.

7. Calorimetric measurements on the aluminum alloy containing 0.0068 at. % copper have revealed two distinct patterns of energy release during recovery annealing. This is in agreement with earlier investigations on recovery in aluminum.

8. It has been suggested that these two recovery stages correspond to (a) the reduction in dislocation density within subgrains and the rearrangement into more stable configurations of dislocations located in the subgrain boundaries; and (b) growth of subgrains subtending small misorientation angles with respect to their neighbors.

ACKNOWLEDGMENTS

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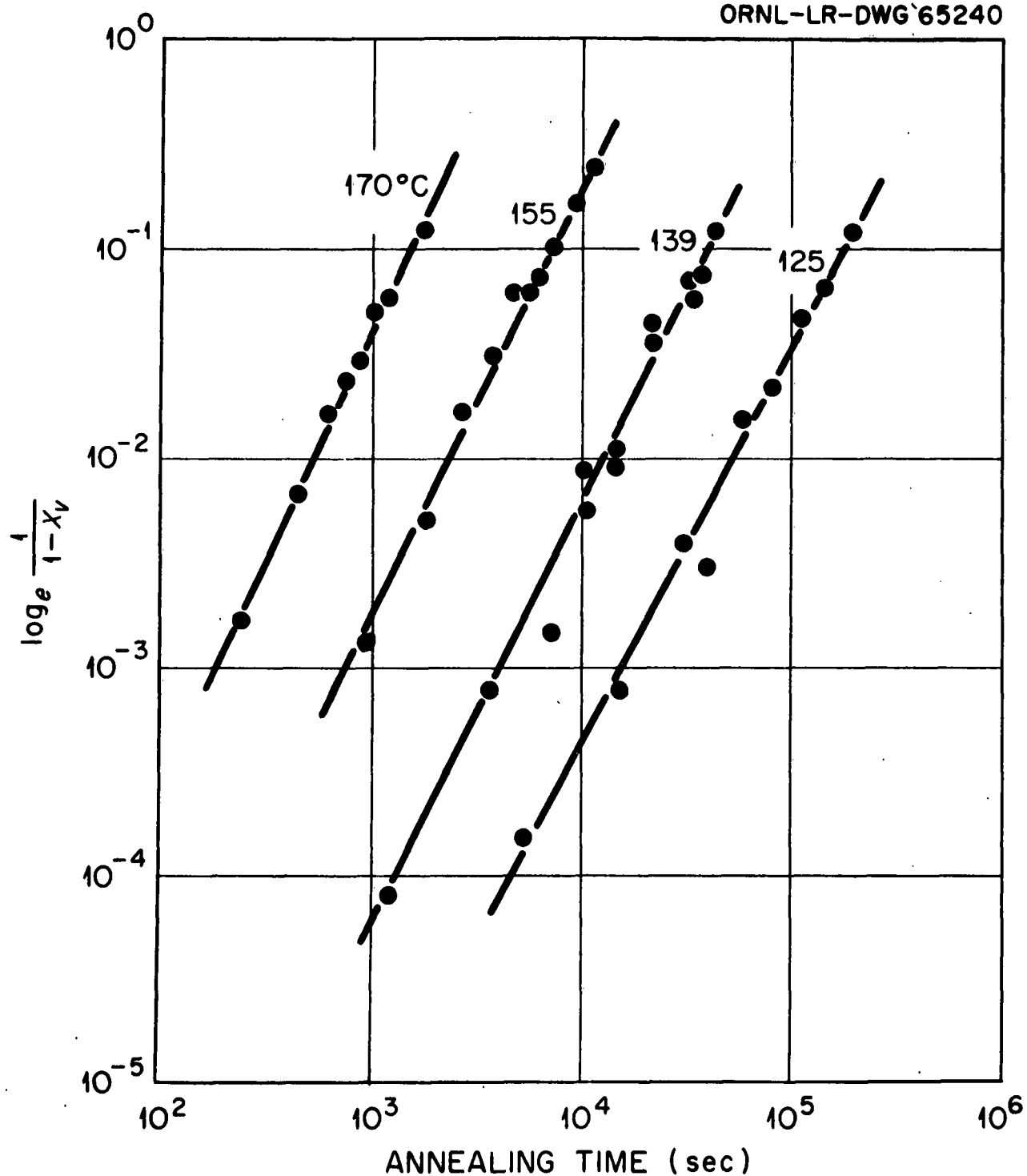
Figure 1.   Log n $\dfrac{1}{1 - X_v}$ versus Log Annealing Time for Recrystalli-zation in an Alloy of Zone-Refine Aluminum Containing 0.0034 at. % Copper Deformed 40% by Rolling at $0^{\circ}C$.
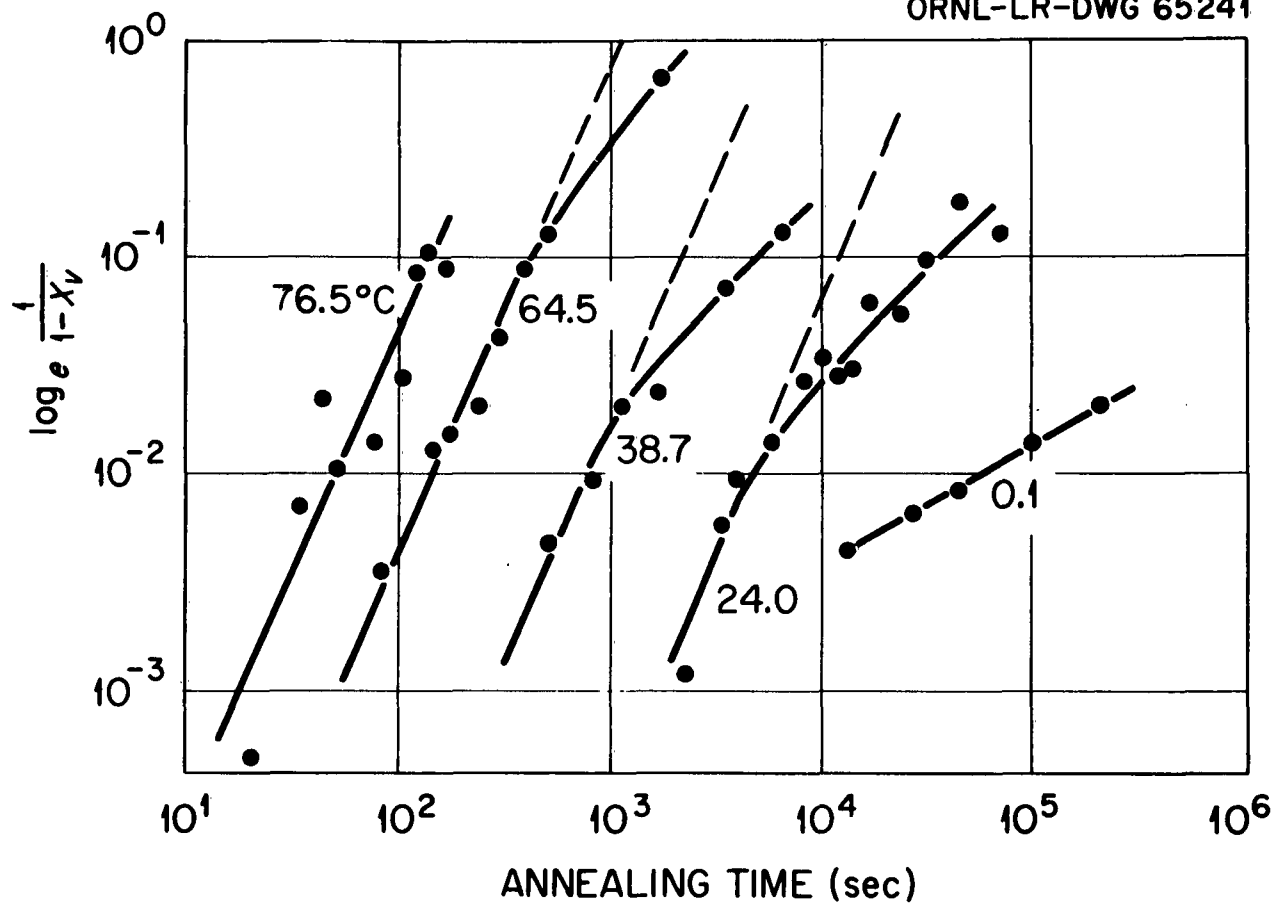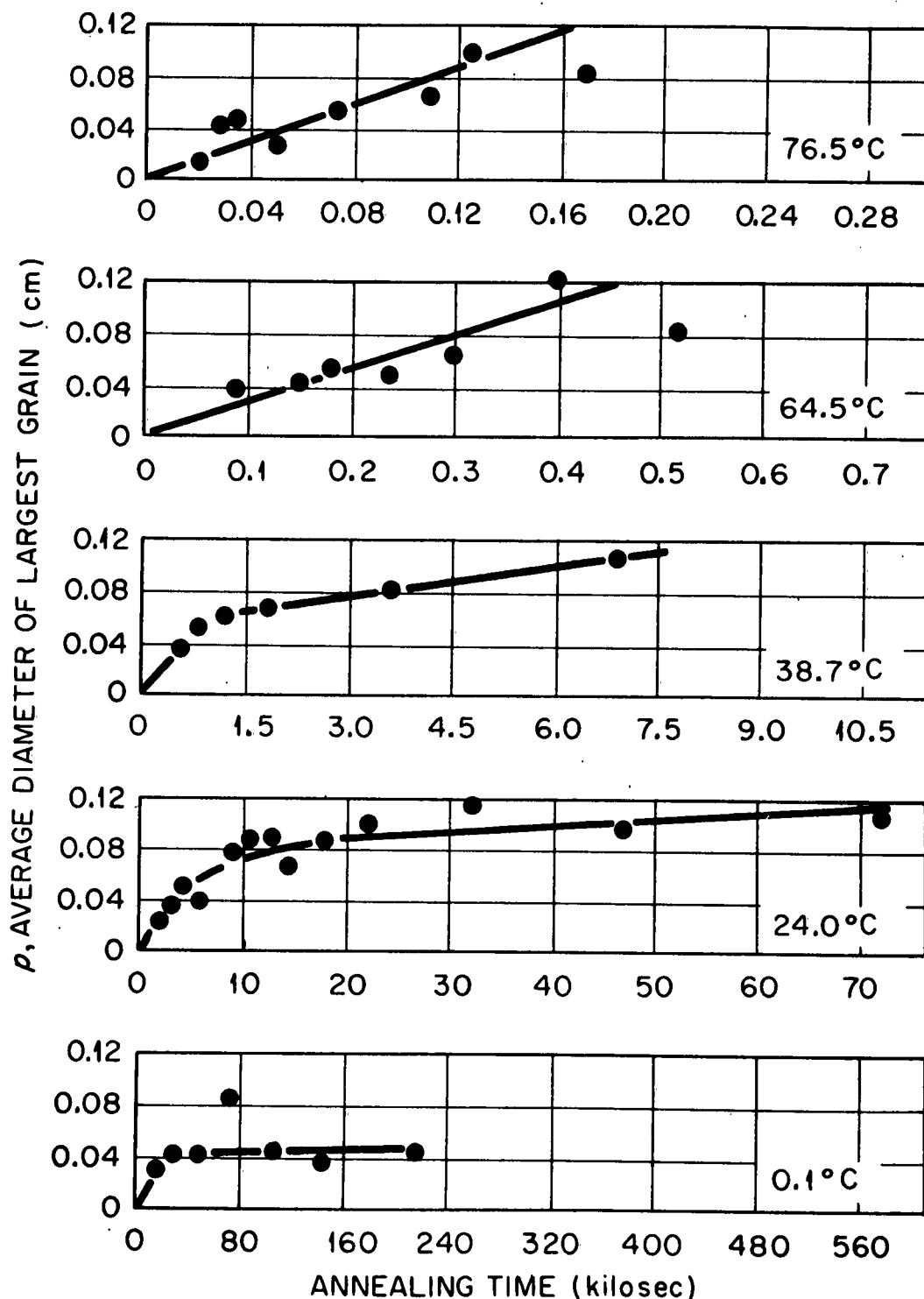
Figure 2. Log n $\dfrac{1}{1 - X_v}$ versus Log Annealing Time for Recrystalli-
zation of Zone-Refined Aluminum Deformed 40% by Rolling
at $0^{\circ}C$.
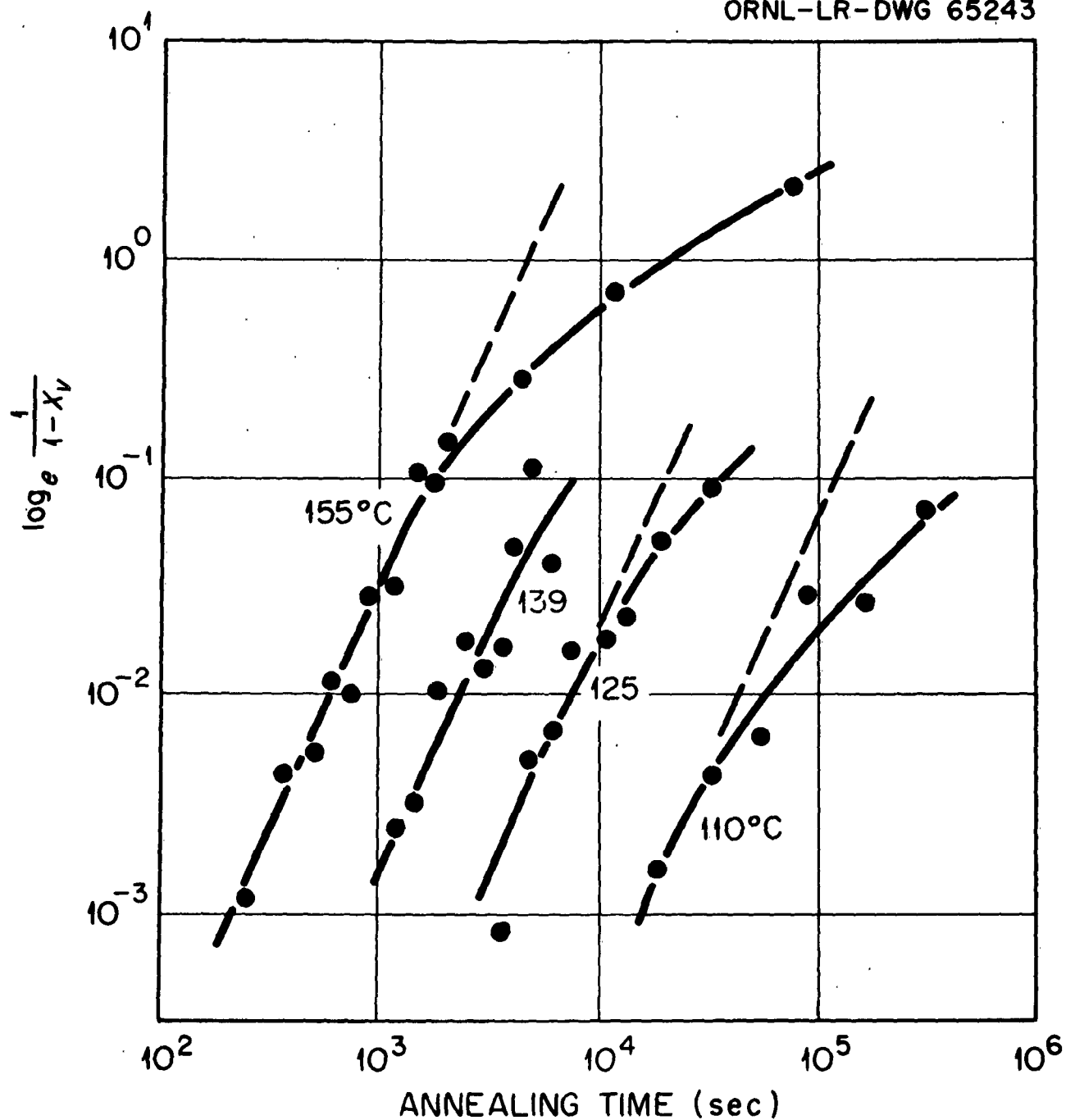
Figure 3. Log n $\dfrac{1}{1 - X_v}$ versus Log Annealing Time for Recrystalli-

zation in an Alloy of Zone-Refined Aluminum Containing

0.0017 at. % Copper Deformed 40% by Rolling at 0°C.
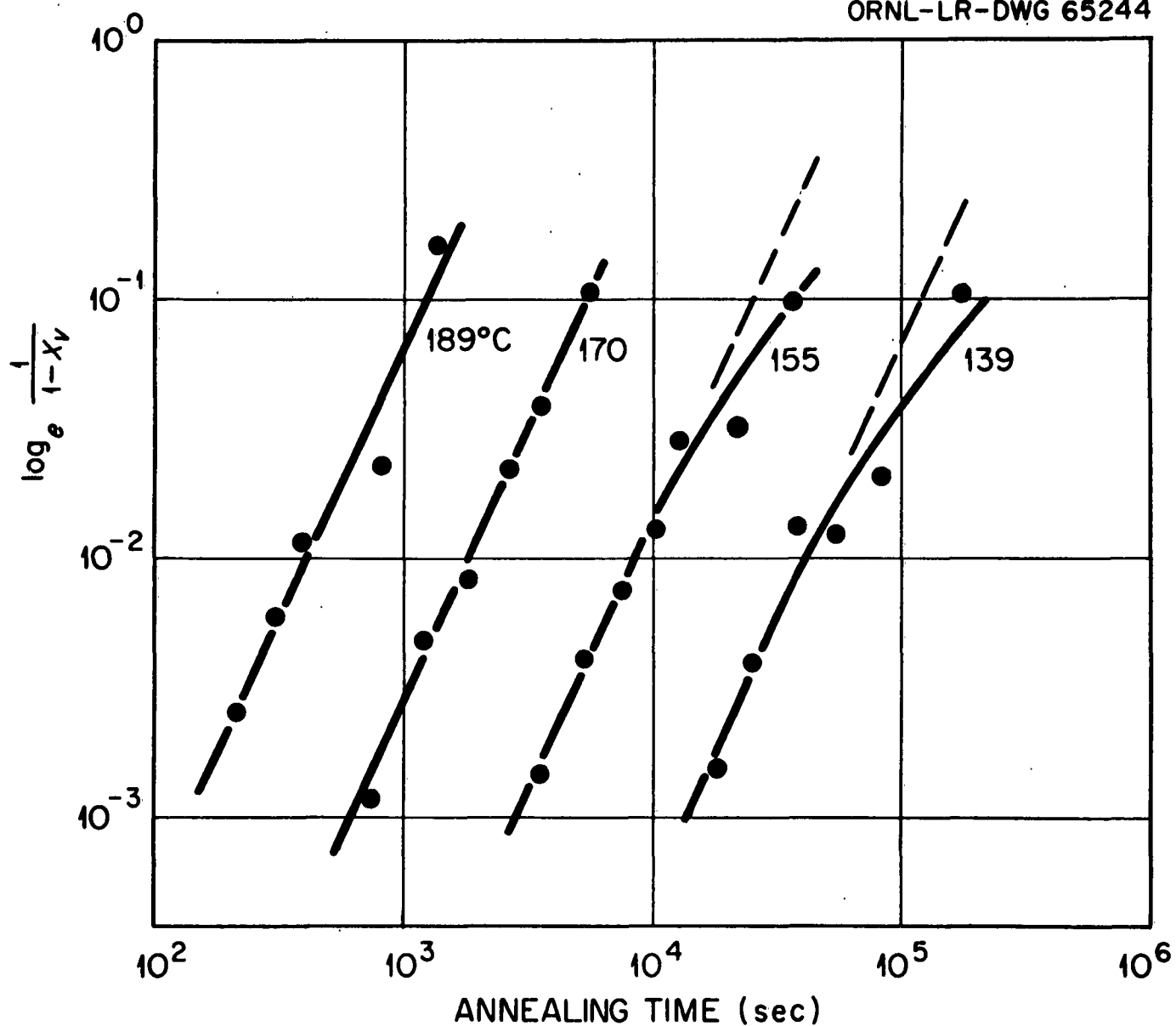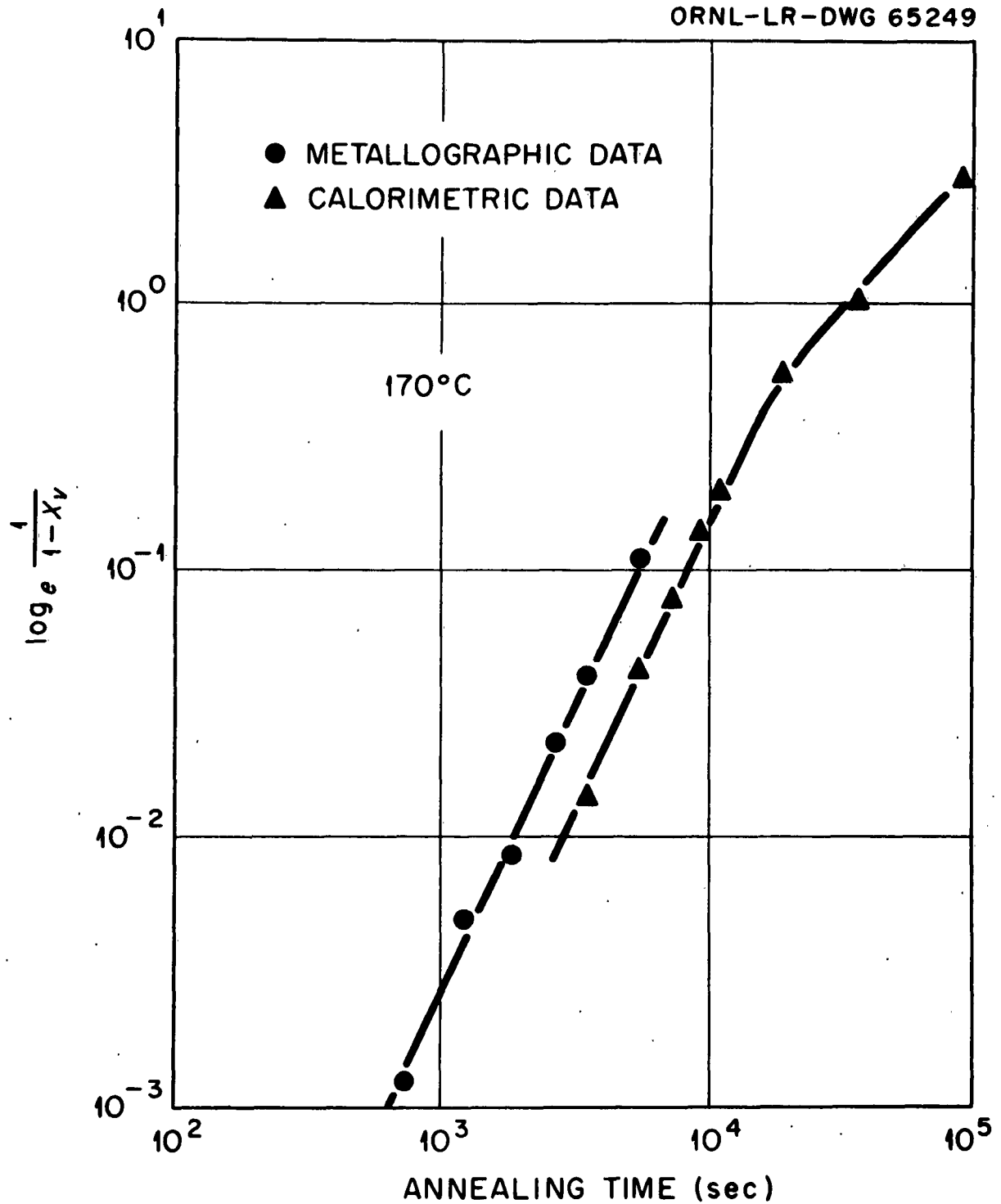
Figure 4. Log n $\dfrac{1}{1 - X_V}$ versus Log Annealing Time for Recrystallization in an Alloy of Zone-Refined Aluminum Containing 0.0068% at. % Copper Deformed 40% by Rolling at 0°C.

Figure 5. Average Diameter of Largest Recrystallized Grain versus Annealing Time During Recrystallization of Zone-Refined Aluminum Deformed 40% by Rolling at 0°C.
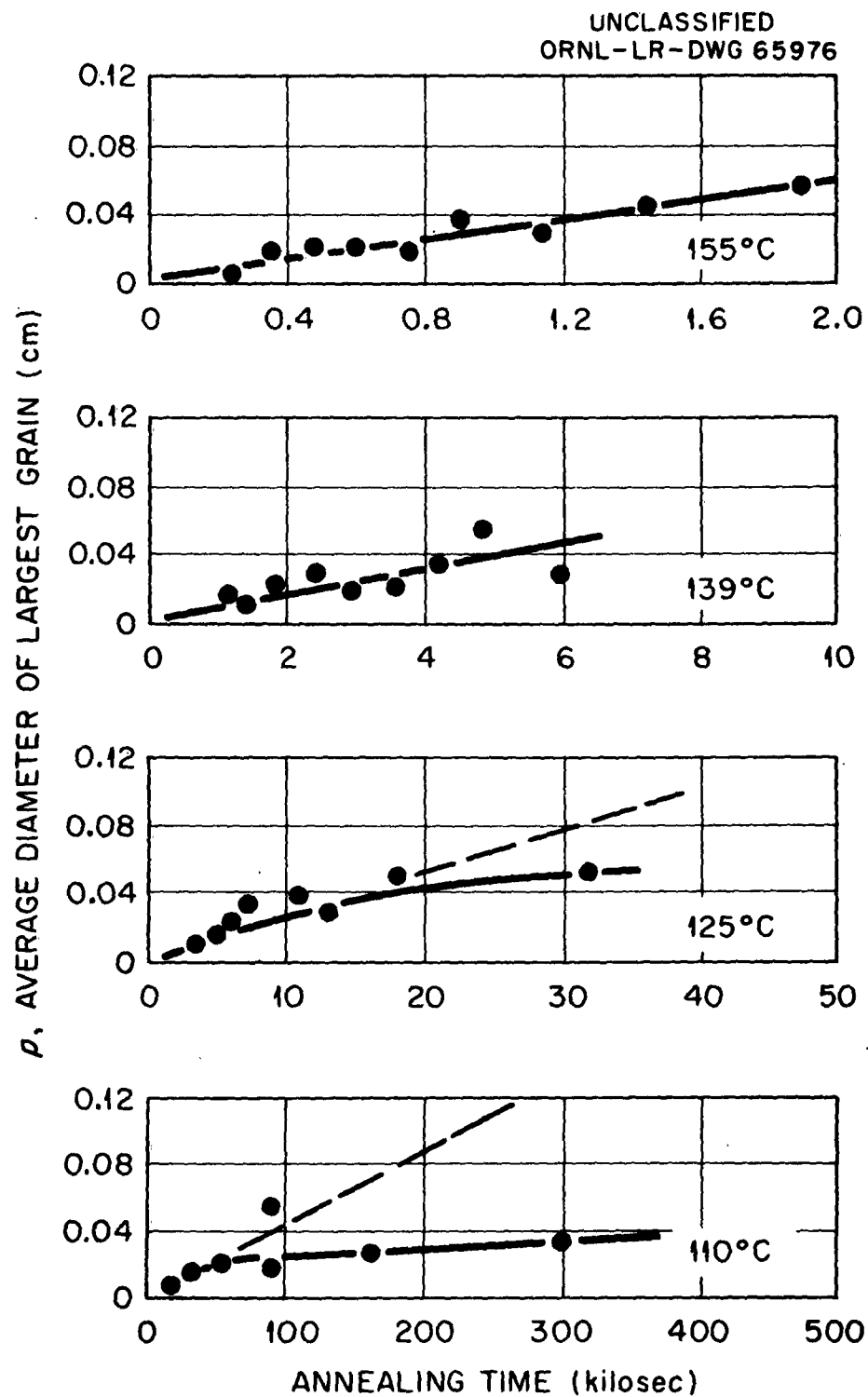
Figure 6. Average Diameter of Largest Recrystallized
Grain versus Annealing Time During Recrystall-
ization of Zone-Refined Aluminum Containing
0.0017 at. % Copper Deformed 40% by Rolling at $0°C$.
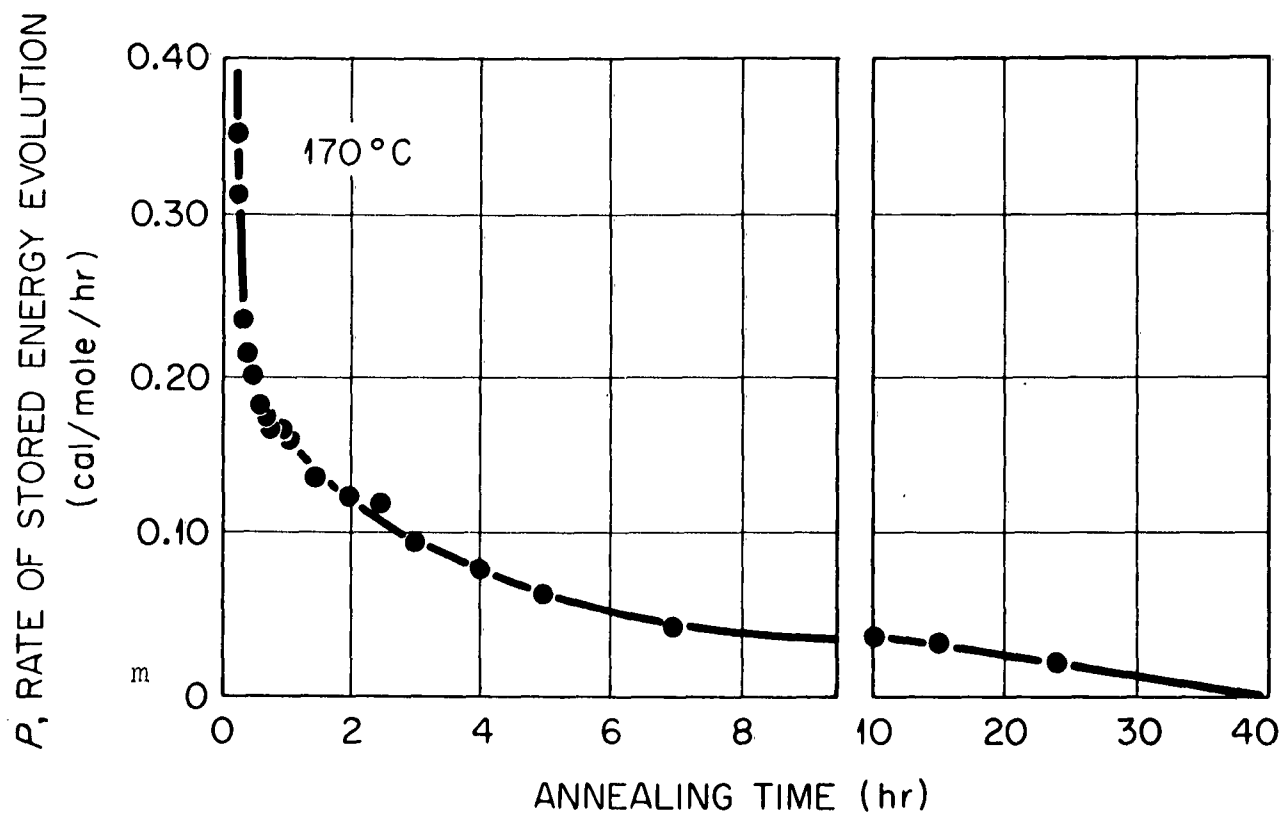
Figure 7. Rate of Stored Energy Evolution versus Annealing Time for a Deformed Specimen of Zone-Refined Aluminum Containing 0.0068 at. % Copper Annealed Directly at 170°C.
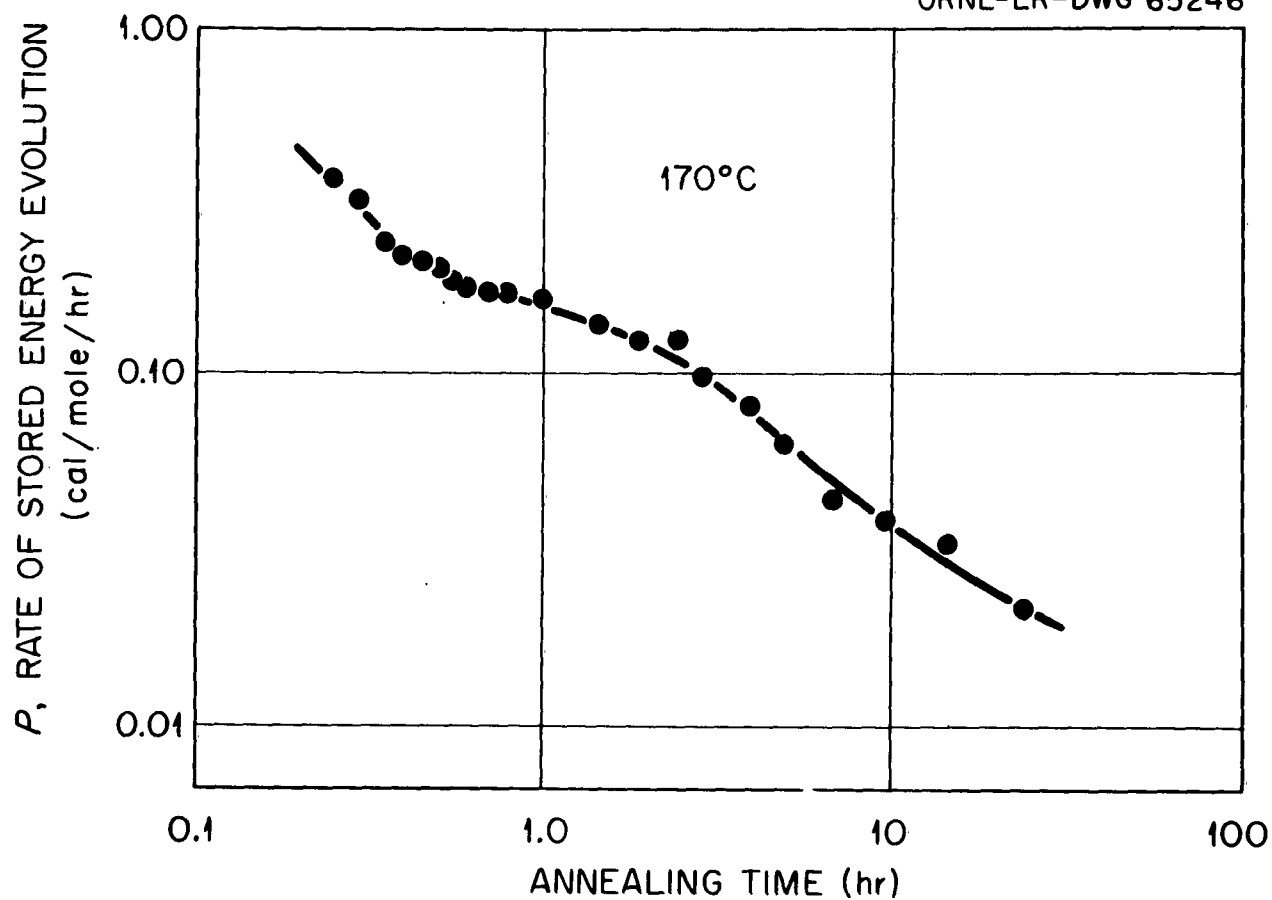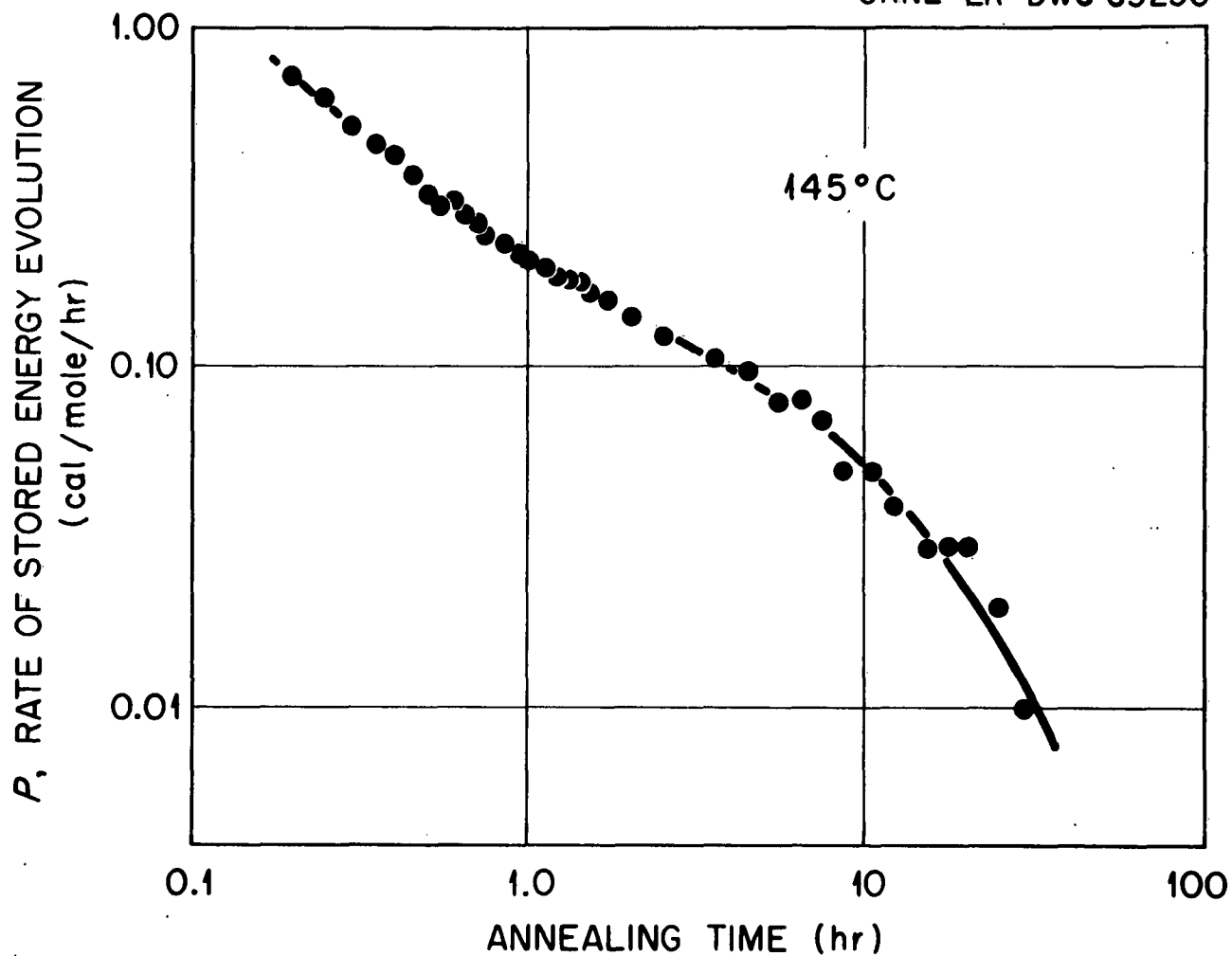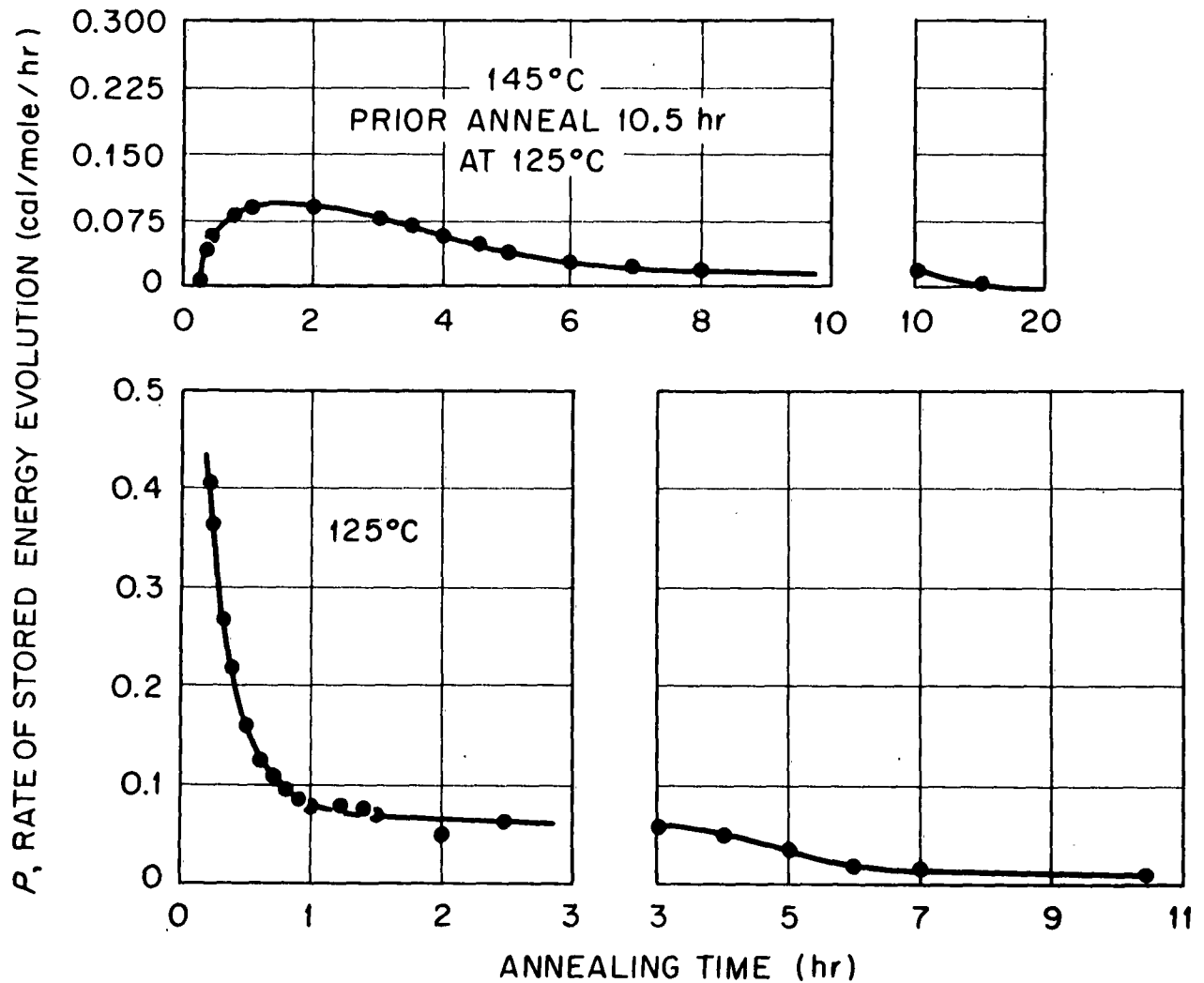
Figure 8. Log Rate of Stored Energy Evolution versus Log Annealing
Time for a Deformed Specimen of Zone-Refined Aluminum
Containing 0.0068 at. % Copper Annealed Directly at 170°C.
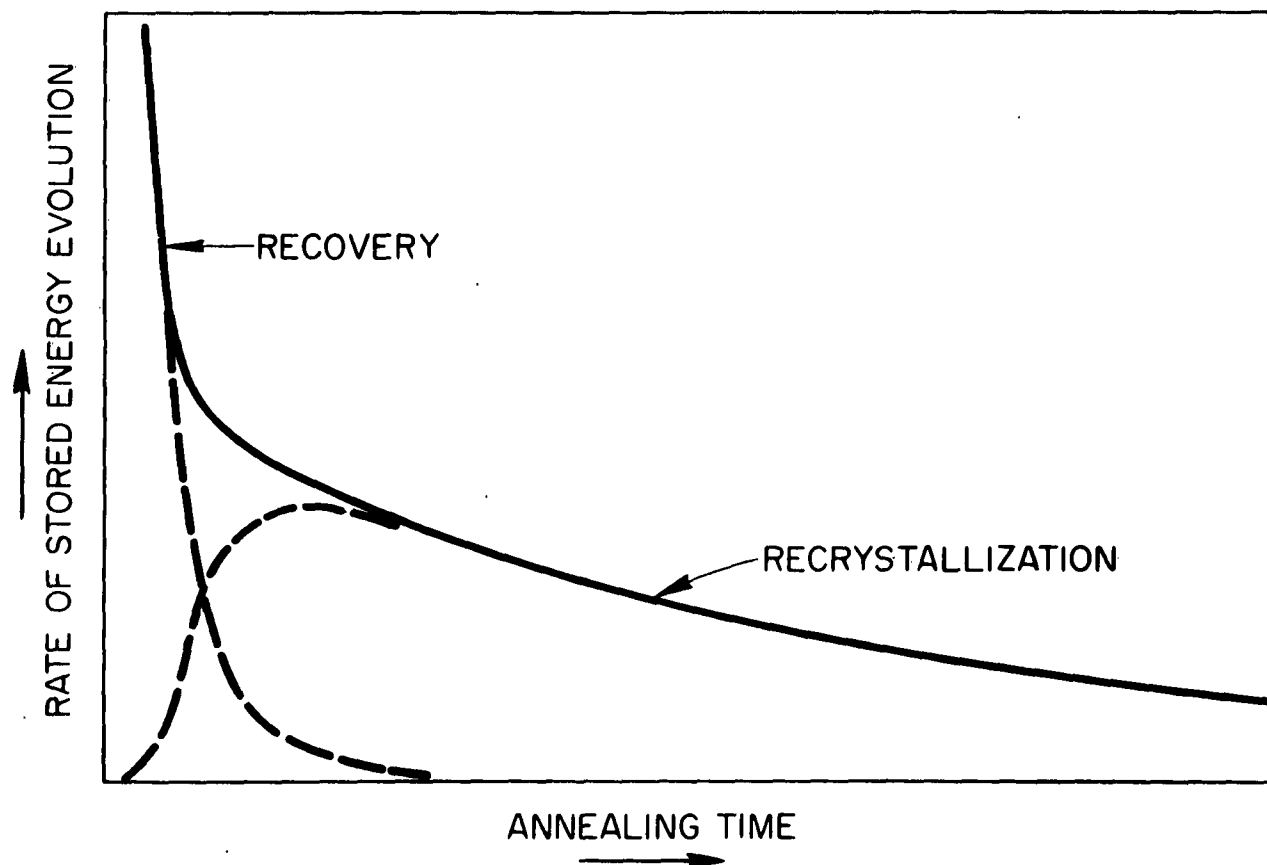
Figure 9. Schematic Illustration of the Overlapping of Recovery
and Recrystallization in the Rate of Stored Energy
Evolution versus Annealing Time Curve of Fig. 7.
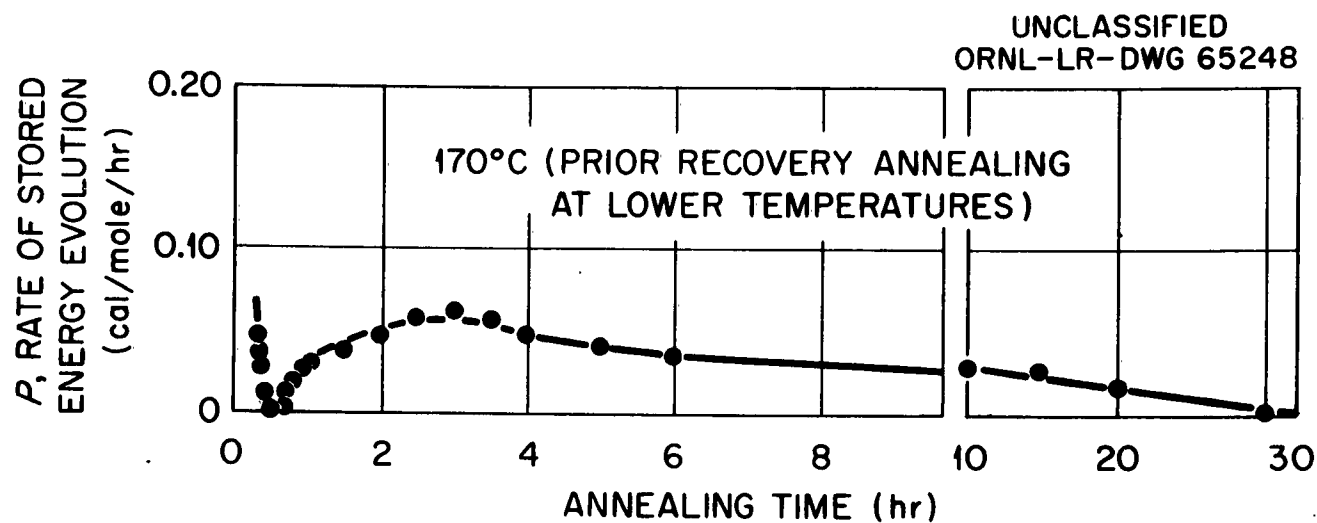
Figure 10. Rate of Stored Energy Evolution versus Annealing Time
During Annealing at 170°C for a Deformed Specimen of
Zone-Refined Aluminum Containing 0.0068 at. T Copper
Which Was Given Several Recovery Anneals at Lower
Temperatures.

Figure 11. Log n $\frac{1}{1 - X_V}$ versus Log Annealing Time for Recrystalli-
zation at $170^{\circ}C$ for the Alloy of Zone-Refined Aluminum
Containing 0.0068 at. % Copper. Circular points -
metallographic data, triangular points - stored energy
evolution data.

Figure 12. Log Rate of Stored Energy Evolution versus Log

Annealing Time for a Deformed Specimen of Zone-Refined

Aluminum Containing 0.0017 at. % Copper Annealed

Directly at 145°C.

Figure 13. Rate of Stored Energy Evolution versus Annealing Time for a Deformed Specimen of Zone-Refined Aluminum Containing 0.0017 at. % Copper Annealed for 10 1/2 hr at 125°C (Lower Curve) with a Subsequent Anneal at 140°C (Upper Curve).
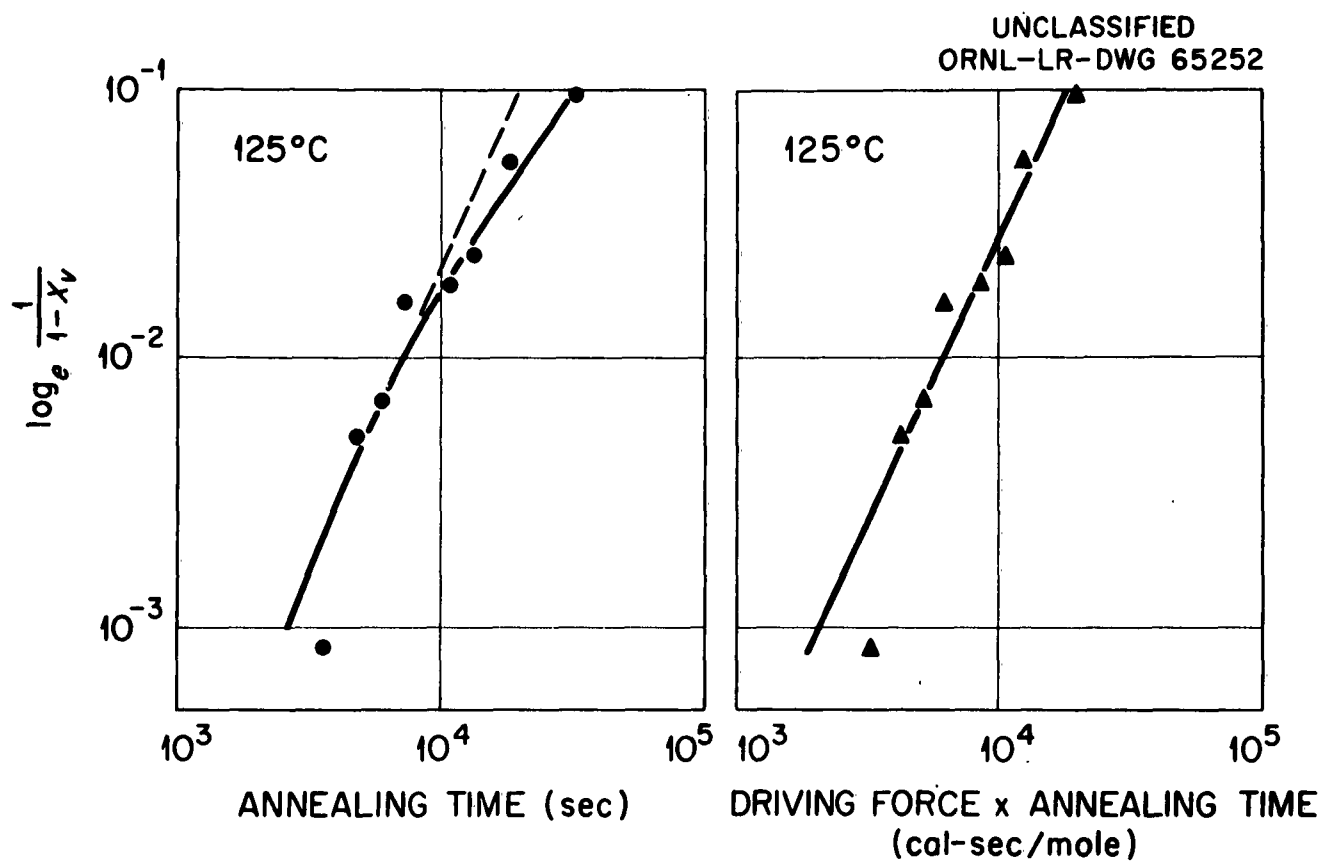
Figure 14. Log n $\frac{1}{1 - X_v}$ versus Annealing Time (Left Hand Curve)
and Log Driving Force x Annealing Time (Right Hand
Curve)for Recrystallization at 125°C in an Alloy of
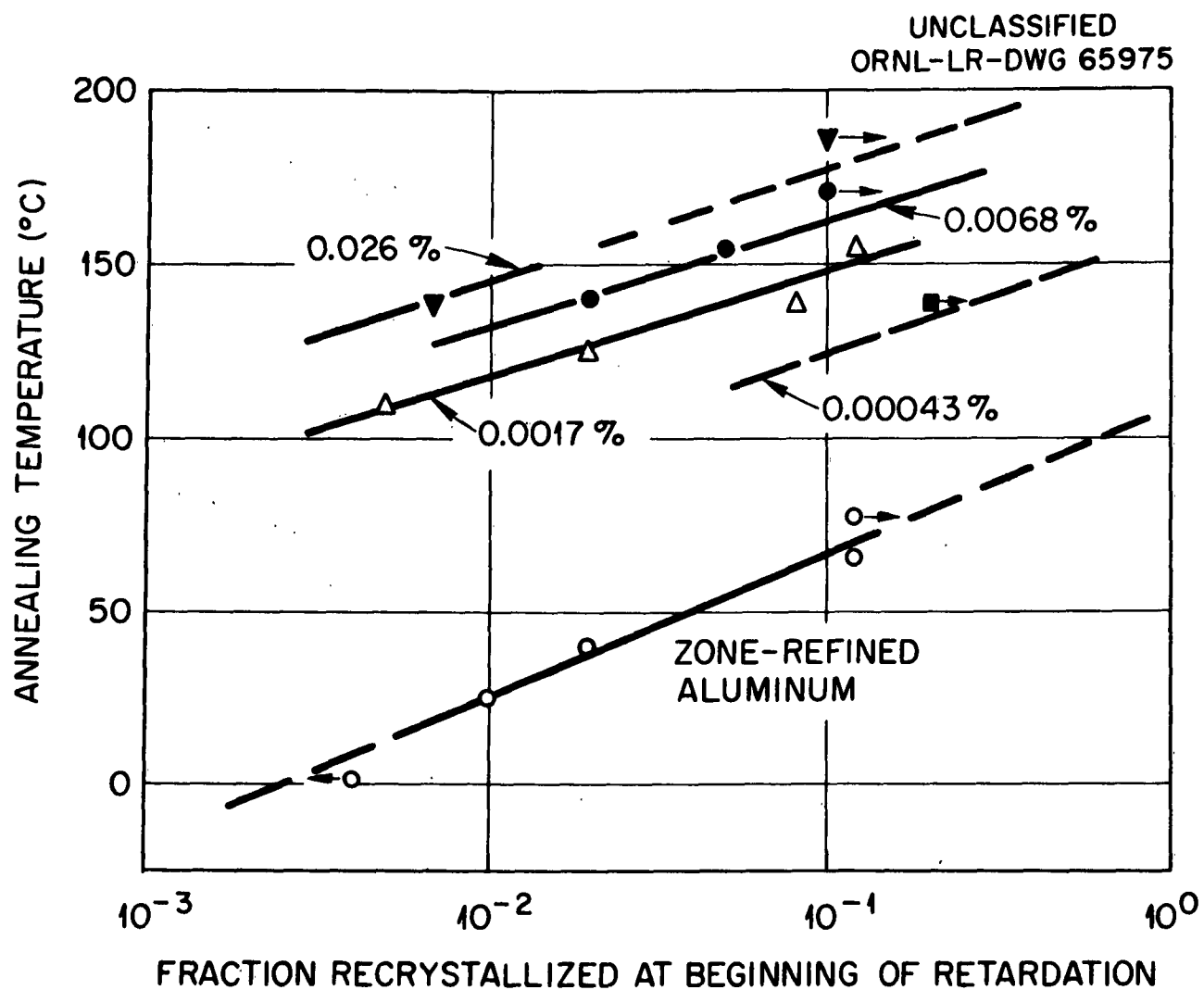Zone-Refined Aluminum Containing 0.0017 at. % Copper.

Figure 15. The Fraction Recrystallized at the Beginning of Retardation
of Recrystallization versus Annealing Temperature for Zone-
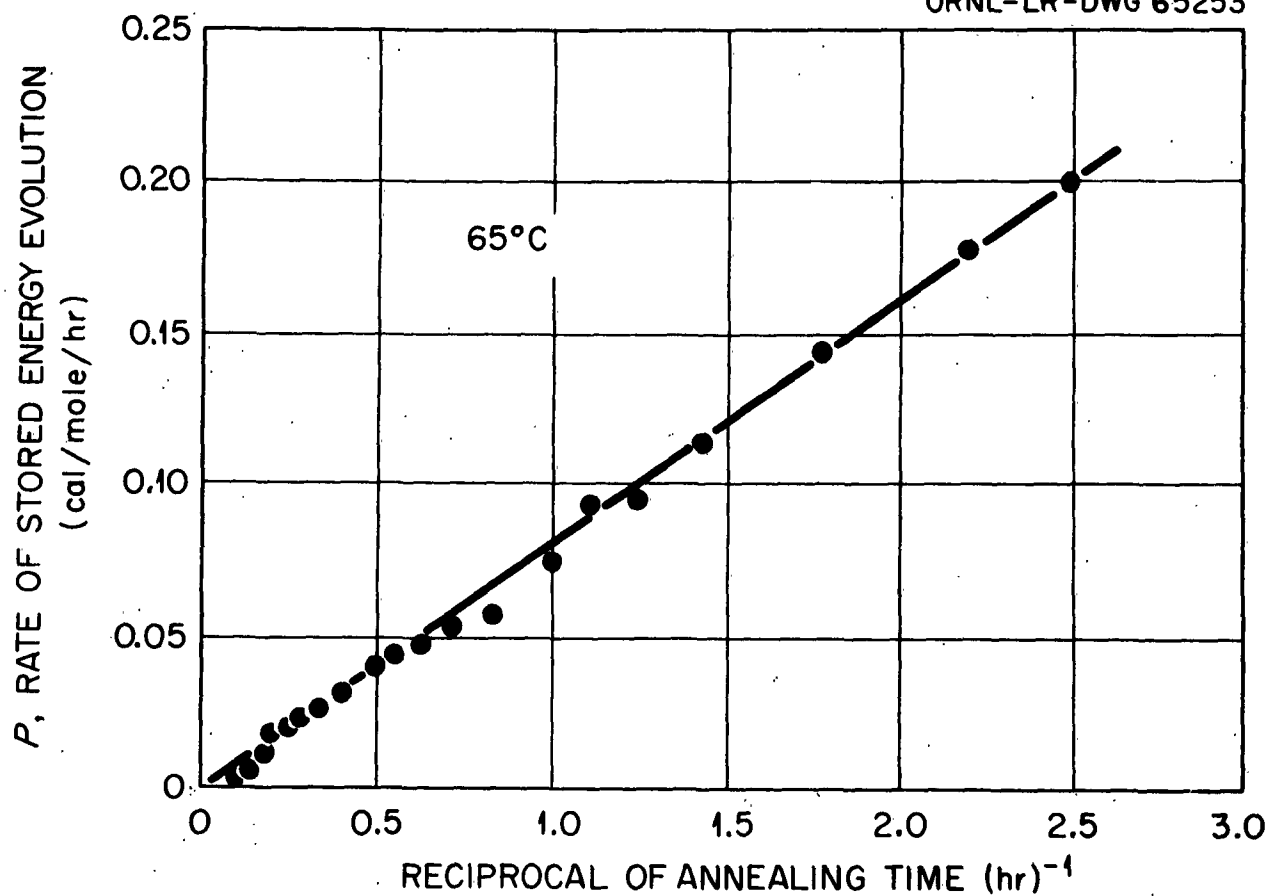Refined Aluminum and Some of the Aluminum-Copper Alloys.

Figure 16. Rate of Stored Energy Evolution versus Reciprocal of Annealing Time for a Deformed Specimen of Zone-Refined Aluminum Containing 0.0068 at. % Copper Annealed at 65°C.
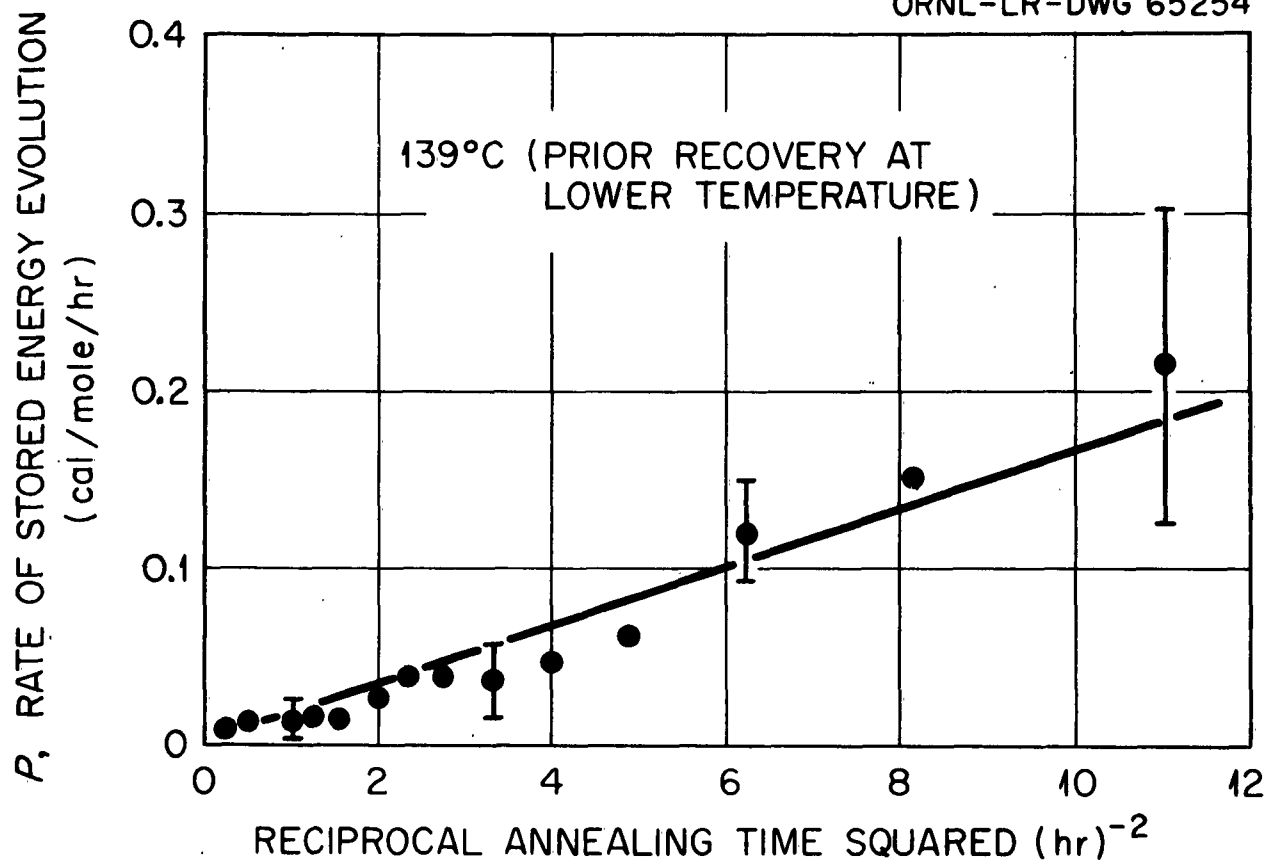
Figure 17. Rate of Stored Energy versus Reciprocal of Annealing

Time Squared for a Deformed Specimen of Zone-Refined

Aluminum Containing 0.0068 at. % Copper Annealed at

139°C after Recovery Annealing at Lower Temperatures.

18. Photomicrograph Depicting the Growth of a Recrystallized Grain into the Deformed Matrix. Electropolished and Anodized. Polarized light. 250X.